

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 241 232 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:

18.09.2002 Bulletin 2002/38

(51) Int Cl.7: **C09B 45/14, C09D 11/00,**
B41M 5/00

(21) Application number: 00985801.0

(86) International application number:
PCT/JP00/09041

(22) Date of filing: 20.12.2000

(87) International publication number:
WO 01/048090 (05.07.2001 Gazette 2001/27)

(84) Designated Contracting States:
DE GB

(72) Inventors:

- **YAMADA, Masahiro, Mitsubishi Chem. Corp.**
Yokohama-shi, Kanagawa 227-0033 (JP)
- **YONEYAMA, Tomio, Mitsubishi Chem. Corp.**
Yokohama-shi, Kanagawa 227-0033 (JP)
- **CHINO, Tomohiro, Mitsubishi Chem. Corp.**
Yokohama-shi, Kanagawa 227-0033 (JP)

(30) Priority: 24.12.1999 JP 36709399

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
81675 München (DE)

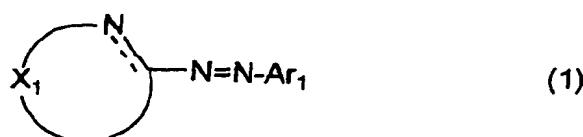
04.07.2000 JP 2000202239

(71) Applicant: **MITSUBISHI CHEMICAL**
CORPORATION
Chiyoda-ku, Tokyo 100-0005 (JP)

(54) **METAL CHELATE DYESTUFF FOR INK JET RECORDING AND WATER-BASE INK JET RECORDING FLUID CONTAINING THE SAME**

(57) The present invention provides a dyestuff good at the cleanness of color tone, light resistance, indoor discoloring and fading property, solubility, storage stability, and the like, when the dyestuff is used as a water soluble dyestuff for inkjet recording.

That is, a metal chelated dyestuff for inkjet recording which is a water soluble azo metal chelated compound formed from an azo compound represented by the following general formula (1) and a metal element:



(where general formula (1) represents an azo dyestuff compound having at least one or more hydrophilic groups in a molecule, X₁ represents plural atoms required for forming at least one 5- to 7-membered heterocyclic ring, the heterocyclic ring containing X₁ being a heterocyclic ring other than a pyridine ring. The heterocyclic ring containing X₁ may have substituent(s) on the heterocyclic ring, the substituent(s) on the heterocyclic ring may form a condensed ring through further condensation. The condensed heterocyclic ring containing X₁ may be substituted. Ar₁ represents naphthyl group having a chelating group.)

EP 1 241 232 A1

Description**Technical Field**

5 [0001] The present invention relates to a water soluble dyestuff for inkjet recording and an aqueous inkjet recording liquid using the same. More specifically, it relates to a metal chelated dyestuff comprising a water soluble azo metal chelated compound suitable for inkjet recording and an aqueous inkjet recording liquid using the same.

Background Art

10 [0002] The recording by blowing drops of recording liquid containing a water soluble dye such as a direct dye or an acid dye from a minute orifice, so-called inkjet recording method, has been practically used.

[0003] With regard to the recording liquid, it is required to exhibit fast fixing to a recording paper widely used at 15 general office work such as a paper for PPC (plain paper copier), i.e., a paper for electrophotography, fanhold paper (a continuous paper for computer, etc.), or the like, and also a good print quality of a printed matter, that is, no blotting, and a clear outline. In addition, it is necessary to be excellent in stability during storage as a recording liquid. Therefore, the solvents which are possible to use are strictly limited.

[0004] With regard to the dye for the recording liquid, it is required that it has a sufficient solubility for the above 20 limited solvents, and, in addition, is stable as a recording liquid even when it has been stored for a long period of time, and a printed image has high saturation and density, as well as the dye is excellent in water resistance, light resistance and indoor discoloring and fading property.

[0005] On the other hand, for forming a full color image in the inkjet recording method, using inks of three primary 25 colors of yellow (Y), magenta (M) and cyan (C) or four colors wherein black (B) is additionally used, an image is formed by controlling the discharging amount of each ink through the mixing of these colors on a material to be recorded. Furthermore, at the formation of a full color image, it is necessary to express not only difference of colors but also shade of colors. The shade part is usually formed by the use of two or more inks different in concentration of dyestuff. [0006] However, with regard to the conventional dyestuffs for inkjet, there is a problem of fading of an image caused 30 by light irradiation, that is, poor light resistance. In particular, it is a problem that a pale color part where an ink low in concentration of dyestuff is used exhibits a poor light resistance. Thus, it is desired to develop a dyestuff for inkjet which satisfies these many requirements at the same time.

[0007] In particular, as the magenta dyestuff to be used in the recording liquid, a metal-free direct dye (C.I. DR-227) 35 and an acid dye (C.I. AR-249) which are commercially available dyes are hitherto employed (by the way, "C.I." means "Color Index", "AR" means "Acid Red", and "DR" means "Direct Red".).

[0008] A direct dye is unclear in color tone, but an acid dye showing a clear color tone tends to exhibit an inferior 40 light resistance. Moreover, heretofore, a metal-containing azo dye has a good light resistance but exhibits a somber color tone and poor clearness. Therefore, it is desired to develop a dyestuff for inkjet which satisfies both the color tone and light resistance.

[0009] Japanese Patent Laid-Open No. 42775/1982 discloses an aqueous ink for inkjet printing wherein at least one 45 kind of 5-hydroxypyrazole azo dye having an azo group at the 4-position or complex salt dye thereof with copper, nickel or cobalt. However, the bonding position of the pyrazole ring to the azo group of the dye described therein is different from that in the general formula (1) of the invention.

[0010] Japanese Patent Laid-Open No. 259331/1998 discloses an aqueous inkjet recording liquid which contains a 50 water soluble metal complex formed from a benzene azo compound and at least one kind of metal selected from nickel, cobalt, chromium or copper. However, the metal complex is different from the compound of the general formula (1) of the invention in view that the complex does not have a naphthalene ring.

[0011] Japanese Patent Laid-Open No. 140367/1999 discloses an ink composition containing a magenta dye ligand of 55 4-hydroxy-3-(2'-pyridylazo)-1-(sulfo substituted)naphthalene which coordinates to a polyvalent metal ion, and an ink vehicle. However, there is a difference in view that the compound of the general formula (1) of the invention is an azo compound having no pyridine ring.

[0012] These dyestuffs described in the known literatures do not always satisfy the properties required for the dyestuff for inkjet printing such as clearness of color tone, light resistance, indoor discoloring and fading property, solubility, storage stability, and the like, sufficiently.

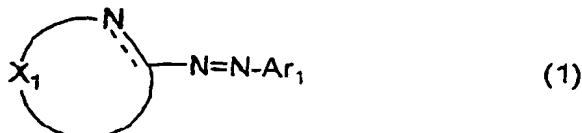
[0013] An object of the invention is to provide a water soluble dyestuff for inkjet printing which results in a good print 55 quality even at printing on a plain paper and also a clear color tone with a high density, an excellent light resistance, small indoor discoloring and fading of a printed image, and exhibits a good solubility or stability during long time storage of the dyestuff, and an aqueous inkjet printing liquid using the same.

Disclosure of the Invention

[0014] The present inventors have achieved the above object by the use of a water soluble dyestuff which is an azo chelated compound of a specific azo compound with a metal element.

[0015] Namely, the gist of the invention is a metal chelated dyestuff for inkjet recording which is a water soluble azo metal chelated compound formed from an azo compound represented by the following general formula (1) and a metal element, and an aqueous ink jet recording liquid which contains at least one kind of the dyestuff selected from the metal chelated dyestuff and an aqueous medium:

10

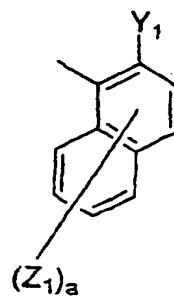
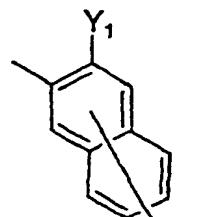
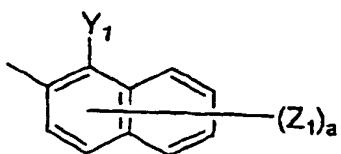


15

(where general formula (1) represents an azo dyestuff compound having at least one or more hydrophilic groups in a molecule, X_1 represents plural atoms required for forming at least one 5- to 7-membered heterocyclic ring, the heterocyclic ring containing X_1 being a heterocyclic ring other than pyridine ring. The heterocyclic ring containing X_1 may have substituent(s) on the heterocyclic ring, the substituent(s) on the heterocyclic ring may form a condensed ring through further condensation. The condensed heterocyclic ring containing X_1 may be substituted. Ar_1 represents a naphthyl group represented by the following general formulae (2) - (4). Y_1 represents a chelating group, Z_1 represents any substituent which may be different from each other, and Z_1 represents an integer of 0 to 6.)

20

25



30

(2)

(3)

(4)

35

40

Best Mode for Carrying out the Invention

[0016] The following will explain the present invention in detail.

[0017] The metal chelated dyestuff of the invention is a water soluble azo metal chelated compound formed from an azo compound represented by the above general formula (1) and a metal element.

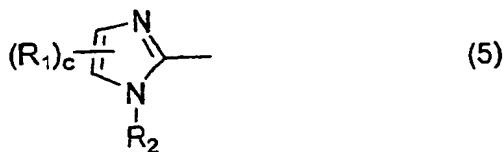
[0018] X_1 represents two or more atoms necessary for forming at least one 5- to 7-membered heterocyclic ring but the heterocyclic ring containing X_1 is a heterocyclic ring other than pyridine ring. The heterocyclic ring containing X_1 is preferably imidazole ring, pyrazole ring, isoxazole ring, thiazole ring, thiadiazole ring, pyridazine ring, pyrimidine ring, pyrazine ring, benzothiazole ring, benzoxazole ring, or benzimidazole ring. Among them, it is preferred that the heterocyclic ring containing X_1 is imidazole ring, pyrazole ring, thiazole ring, or thiadiazole ring.

[0019] The heterocyclic ring containing X_1 may have one or more substituents on the heterocyclic ring, and the substituent(s) on the heterocyclic ring may form a condensed ring through further condensation. In that case, the substituents on the heterocyclic ring each are selected independently from alkyl group which may be substituted (e.g., alkyl group having 1 to 6 carbon atoms such as methyl group, ethyl group, or the like, carboxymethyl group, carboxyethyl group, trifluoromethyl group, or the like), aryl group which may be substituted (preferably aryl group having 6 to 10 carbon atoms, e.g., phenyl group, naphthyl group, or the like), aralkyl group which may be substituted (benzyl group or the like, preferably aralkyl group having 7 to 10 carbon atoms in total), allyl group which may be substituted

(e.g., vinyl group, 2-propenyl group, or the like), alkoxy group which may be substituted (preferably alkoxy group having 1 to 6 carbon atoms, e.g., methoxy group, ethoxy group, or the like), aryloxy group which may be substituted (e.g., phenoxy group, or the like), acyloxy group which may be substituted (preferably alkanoyloxy group having 2 to 7 carbon atoms such as acetoxy group, benzoyloxy group, or the like), alkoxy carbonyl group which may be substituted (preferably alkoxy carbonyl group having 2 to 7 carbon atoms, e.g., methoxycarbonyl, ethoxycarbonyl, or the like), aryloxy carbonyl group which may be substituted (e.g., phenoxy carbonyl group, naphthoxy carbonyl group, or the like), carbonyl group which may be substituted, acyl group which may be substituted (e.g., acyl group having 2 to 10 carbon atoms such as acetyl group, or the like), carboxyl group, hydroxyl group, cyano group, acylamino group which may be substituted (e.g., alkanoylamino group having 2 to 7 carbon atoms such as acetylamino group, benzoylamino group, or the like), nitro group, halogen atom (e.g., chlorine atom, bromine atom, fluorine atom, or the like), phosphono group, sulfo group, mercapto group, alkylthio group which may be substituted (e.g., alkylthio group having 1 to 6 carbon atoms such as methylthio group or ethylthio group, or the like), alkylsulfoxyl group which may be substituted (e.g., alkylsulfoxyl group having 1 to 6 carbon atoms such as methylsulfoxyl group or ethylsulfoxyl group, or the like), alkylsulfonyl group which may be substituted (e.g., alkylsulfonyl group having 1 to 6 carbon atoms such as methylsulfonyl group or ethylsulfonyl group, or the like), or thiocyanato group.

[0020] Among them, a metal chelated dyestuff is preferred wherein, in the general formula (1), the heterocyclic ring containing X_1 is preferably represented by the following general formula (5), (6), (7) or (8).

20

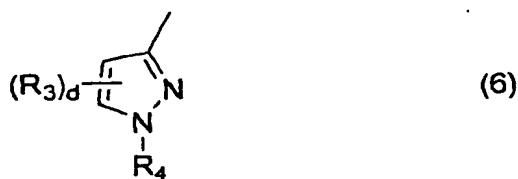


25

(where R_1 may be different from each other and is a group selected from alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carboxyl group, carbamoyl group which may be substituted, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, mercapto group, alkylthio group which may be substituted and thiocyanato group, or the like. R_1 may further form a condensed ring together with an imidazole ring. c represents an integer of 0 to 2. R_2 group, R_1 represents hydrogen atom, alkyl group which may be substituted and allyl group which may be substituted.)

[0021] In particular, preferred is the case that R_1 is an alkoxy carbonyl group which may be substituted, carboxyl group, or cyano group and preferred is the case that R_2 is hydrogen atom or alkyl group which may be substituted. Most preferred is the case that c is 2, both of the two R_1 's are cyano groups, and R_2 is hydrogen atom or alkyl group which may be substituted.

40



45

(where R_3 may be different from each other and represents alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carboxyl group, carbamoyl group which may be substituted, hydroxyl group, cyano group or sulfo group, d represents an integer of 0 to 2. R_4 represents hydrogen atom, alkyl group which may be substituted or aryl group which may be substituted.)

55

5



(7)

(where R_5 may be different from each other and represents alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carboxyl group, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, alkylthio group which may be substituted or arylthio group which may be substituted, and R_5 may further form a condensed ring together with thiazole ring, e represents an integer of 0 to 2)

[0022] Preferred are the case that R_5 is alkyl group which may be substituted, the case that $e = 0$ and R_5 is absent, or the case that R_5 forms a condensed ring together with thiazole ring.

20



(8)

25 (where R_6 represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, mercapto group, alkylthio group which may be substituted, alkylsulfonyl group which may be substituted or alkylsulfonyl group which may be substituted.)

[0023] R_6 is preferably hydrogen atom or alkyl group which may be substituted.

30 [0024] Among the heterocyclic rings represented by the above general formula (5), (6), (7) or (8), preferred is imidazole ring represented by the general formula (5).

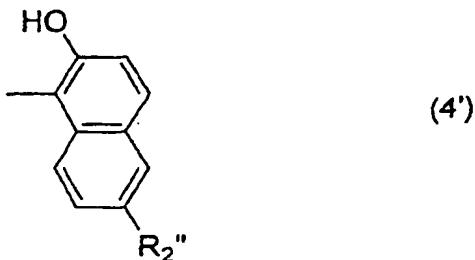
[0025] Moreover, Ar_1 in the general formula (1) is naphthyl group represented by the general formula (2), (3) or (4), and Y_1 is a chelating group. Y_1 is preferably hydroxyl group, carboxyl group, amino group which may be substituted (e.g., amino group, methylamino group, bis(2-hydroxyethyl)amino group, or the like), sulfo group, carbamoyl group, alkoxy group which may be substituted (e.g., methoxy group, carbonyl group, 2-hydroxyethoxy group, or the like), alkylthio group which may be substituted (e.g., methylthio group, 2-hydroxyethylthio group, or the like), alkylsulfonylamino group which may be substituted (e.g., methylsulfonylamino group or the like), or arylsulfonylamino group which may be substituted (e.g., benzenesulfonylamino group or the like). More preferred is the case that Y_1 is hydroxyl group.

[0026] It is preferable that Z_1 in the general formulae (2) to (4), each is independently a group selected from alkoxy group which may be substituted (e.g., alkoxy group having 1 to 6 carbon atoms such as methoxy group or ethoxy group, or the like), aryloxy group which may be substituted (e.g., phenoxy group, or the like), acyloxy group which may be substituted (e.g., alkanoyloxy group having 2 to 7 carbon atoms such as acetoxy group, benzyloxy group, or the like), alkoxy carbonyl group which may be substituted (e.g., alkoxy carbonyl group having 2 to 7 carbon atoms such as methoxycarbonyl, ethoxycarbonyl, or the like), aryloxycarbonyl group which may be substituted (e.g., phenoxy carbonyl group, naphthoxy carbonyl group, or the like), carboxyl group, carbamoyl group which may be substituted (e.g., carbamoyl group, carboxyanilide group which may be substituted (3-sulfo carboxyanilide group or the like), hydroxyl group, amino group which may be substituted (e.g., amino group, alkylamino group having 1 to 6 carbon atoms such as methylamino group, or the like), ureido group, acylamino group which may be substituted (e.g., alkanoylamino group having 2 to 7 carbon atoms such as acetylamino group, benzoylamino group, or the like), alkylsulfonylamino group which may be substituted (e.g., alkylsulfonylamino group having 1 to 6 carbon atoms such as methylsulfonylamino group, or the like), arylsulfonylamino group which may be substituted (e.g., phenylsulfonylamino group, 4-methylphenylsulfonylamino group, or the like), phosphono group, sulfo group, and sulfamoyl group which may be substituted (e.g., sulfamoyl group, N,N-bis(carboxymethyl)sulfamoyl group, or the like). a represents an integer of 0 to 6.

[0027] Z_1 is preferably carboxyl group, carbamoyl group which may be substituted, sulfo group, or sulfamoyl group which may be substituted. a is preferably an integer of 1 to 3, more preferably 1 or 2.

55 [0028] Furthermore, among the naphthyl groups represented by the general formula (2), (3) or (4), preferred is the general formula (2) or (4).

[0029] In particular, most preferred is the naphthyl group of the following general formula (4').



(where R_2'' represents sulfo group or sulfamoyl group which may be substituted.)

[0030] The azo compound represented by the general formula (1) is a compound having at least one hydrophilic group in a molecule other than Y_1 which is a chelating group. Examples of such hydrophilic group include sulfo group, carboxyl group, hydroxyl group, amino group, phosphono group, or the like. Of these, preferred is sulfo group or carboxyl group. It is more preferable that the azo compound represented by the general formula (1) is a compound having 1 to 3 sulfo groups or carboxyl groups in a molecule

[0031] In the invention, examples of the metal forming a chelated compound together with the azo compound represented by the general formula (1) include silver (I), aluminum (III), gold (III), cerium (III, IV), cobalt (II, III), chromium (III), copper (I, II), europium (III), iron (II, III), gallium (II), germanium (IV), indium (III), lanthanum (III), manganese (II), nickel (II), palladium (II), platinum (II, IV), rhodium (II, III), ruthenium (II, III, IV), scandium (III), silicon (IV), samarium (III), titanium (IV), uranium (IV), zinc (II), zirconium (IV), and the like.

[0032] Preferred are nickel (II), cobalt (II, III), and copper (II). More preferred are nickel (II) and copper (II), and most preferred is nickel (II).

[0033] As an anion of the metal salt to be used at the production of the metal complex, a monovalent or divalent anion such as Cl^- , Br^- , CH_3COO^- , SO_4^{2-} , or the like may be mentioned.

[0034] The dyestuff for use in the invention may be used in a form of free acid, as it is, and when the dyestuff is formed as a salt form at the production, it may be used as it is, or may be converted to a desired salt form. Furthermore, a dyestuff wherein part of the acid groups is a salt form or a mixture of a salt-form dyestuff and a free acid-form dyestuff may be used. Examples of such salt form includes salts with alkali metals such as Na, Li, K, etc.; ammonium salts which may be substituted with alkyl group(s) or hydroxyalkyl group(s); or salts with organic amines. Examples of the organic amines include lower alkylamines, hydroxy-substituted lower alkylamines, carboxy-substituted lower alkylamines and polyamines having 2 to 10 alkyleneimine units having 2 to 4 carbon atoms, and the like. In these salt-form cases, the dyestuff is not limited to one kind of form and two or more kinds may be mixed.

[0035] Moreover, in the structure of the dyestuff for use in the invention, when two or more acid groups are contained in one molecule thereof, the two or more acid groups are salt forms or acid forms and may be different from each other.

[0036] As specific examples of the dyestuff include the dyestuffs having structures shown in following Table 1 to Table 6, but the invention is not limited thereto.

40

45

50

55

Table 1

| No. | X_1 | $-\text{Ar}_1$ | Metal compound |
|-----|--------------|----------------|--|
| 1-1 | | | $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ |
| 1-2 | | | $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ |
| 1-3 | | | $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ |
| 1-4 | | | $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ |

Table 1 (Cont'd)

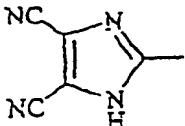
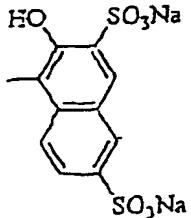
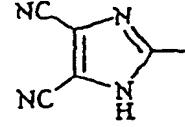
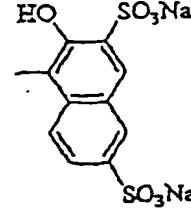
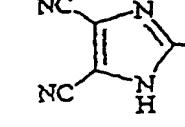
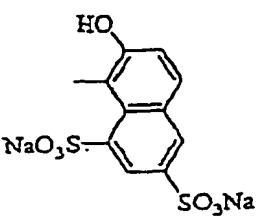
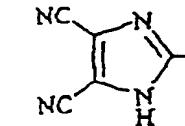
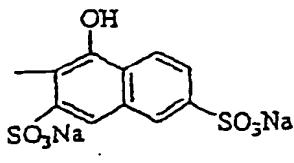
| No. |  | -Ar ₁ | Metal compound |
|-----|---|--|--|
| 1-5 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-6 |  |  | CuCl ₂ · 2 H ₂ O |
| 1-7 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-8 |  |  | NiCl ₂ · 6 H ₂ O |

Table 1 (Cont'd)

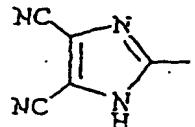
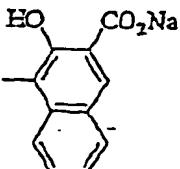
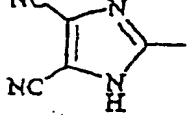
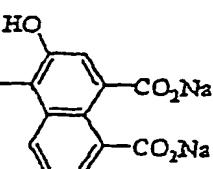
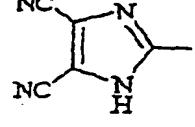
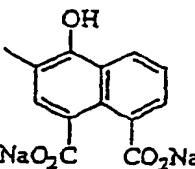
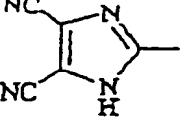
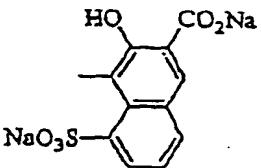
| No. |  | -Ar ₁ | Metal compound |
|------|---|--|--|
| 1-9 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-10 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-11 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-12 |  |  | NiCl ₂ · 6 H ₂ O |

Table 1 (Cont'd)

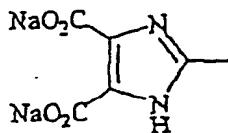
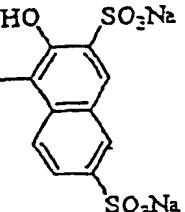
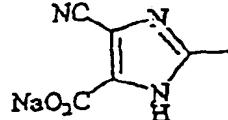
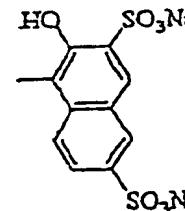
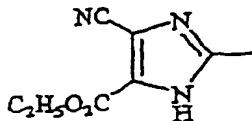
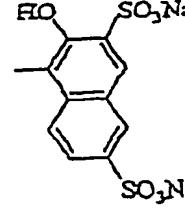
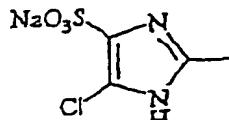
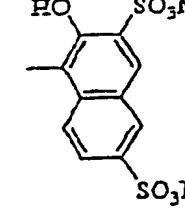
| No. |  | -Ar ₁ | Metal compound |
|------|---|--|--|
| 1-13 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-14 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-15 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-16 |  |  | NiCl ₂ · 6 H ₂ O |

Table 1 (Cont'd)

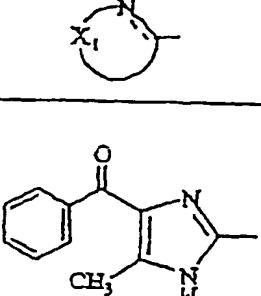
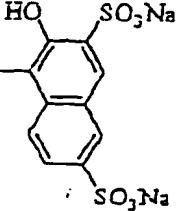
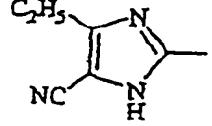
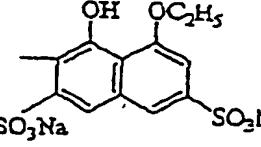
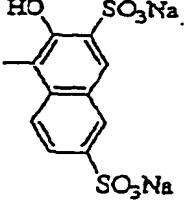
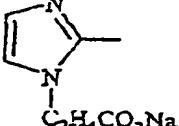
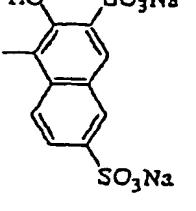
| Na | X ₁ | -Ar ₁ | Metal compound |
|------|---|--|--|
| 1-17 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-18 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-19 |  |  | NiCl ₂ · 6 H ₂ O |
| 1-20 |  |  | NiCl ₂ · 6 H ₂ O |

Table 1 (Cont'd)

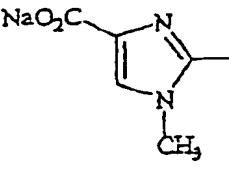
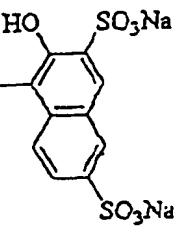
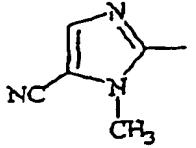
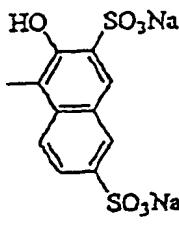
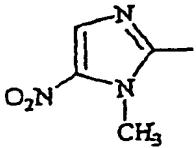
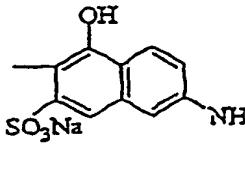
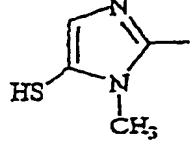
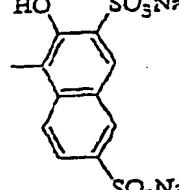
| | Na |  | -Ar ₁ | Metal compound |
|----|------|---|--|--|
| 5 | | | | |
| 10 | 1-21 |  |  | NiCl ₂ · 6 H ₂ O |
| 15 | 1-22 |  |  | NiCl ₂ · 6 H ₂ O |
| 20 | 1-23 |  |  | NiCl ₂ · 6 H ₂ O |
| 25 | 1-24 |  |  | NiCl ₂ · 6 H ₂ O |
| 30 | | | | |
| 35 | | | | |
| 40 | | | | |
| 45 | | | | |
| 50 | | | | |
| 55 | | | | |

Table 1 (Cont'd)

| No. | X_1 | $-Ar_1$ | Metal compound |
|------|-------|---------|----------------------|
| 1-25 | | | $NiCl_2 \cdot 6H_2O$ |
| 1-26 | | | $NiCl_2 \cdot 6H_2O$ |
| 1-27 | | | $NiCl_2 \cdot 6H_2O$ |
| 1-28 | | | $NiCl_2 \cdot 6H_2O$ |

Table 1 (Cont'd)

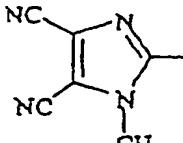
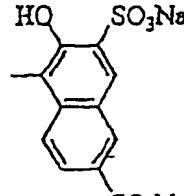
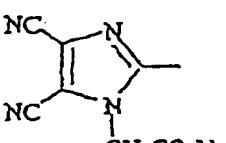
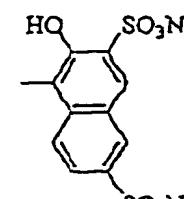
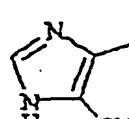
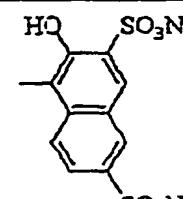
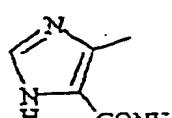
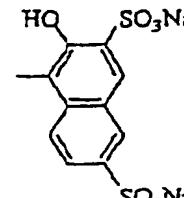
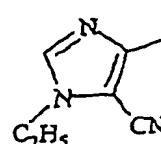
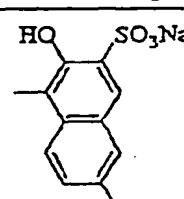
| No. | X_1 | $-Ar_1$ | Metal compound |
|------|---|--|-----------------------|
| 1-29 |  |  | $NiCl_2 \cdot 6 H_2O$ |
| 1-30 |  |  | $NiCl_2 \cdot 6 H_2O$ |
| 1-31 |  |  | $NiCl_2 \cdot 6 H_2O$ |
| 1-32 |  |  | $NiCl_2 \cdot 6 H_2O$ |
| 1-33 |  |  | $NiCl_2 \cdot 6 H_2O$ |

Table 1 (Cont'd)

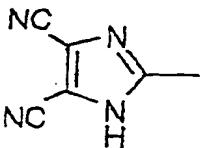
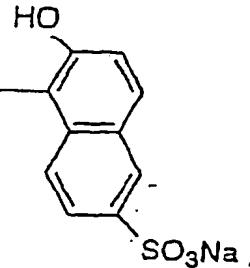
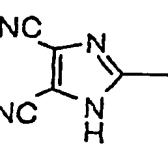
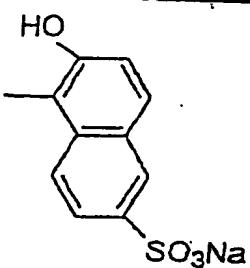
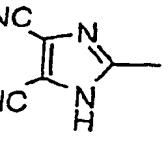
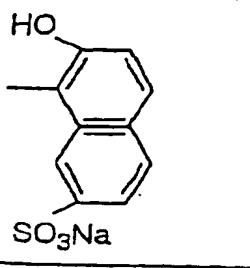
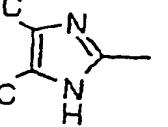
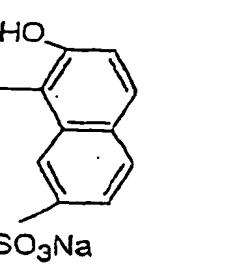
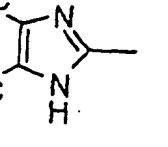
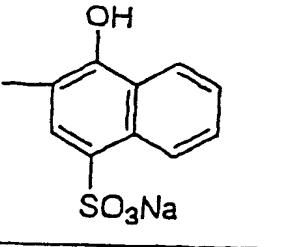
| NO. |  | -Ar ₁ | Metal compound |
|------|---|--|---------------------------------------|
| 1-34 |  |  | NiCl ₂ · 6H ₂ O |
| 1-35 |  |  | CuCl ₂ · 2H ₂ O |
| 1-36 |  |  | NiCl ₂ · 6H ₂ O |
| 1-37 |  |  | CuCl ₂ · 6H ₂ O |
| 1-38 |  |  | NiCl ₂ · 6H ₂ O |

Table 1 (Cont'd)

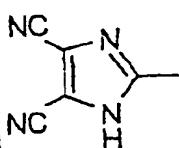
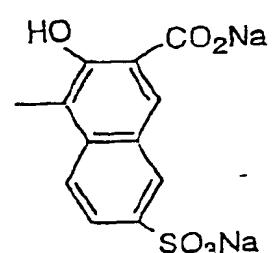
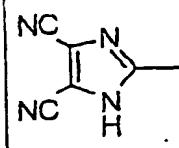
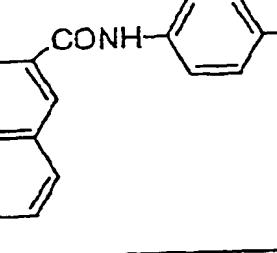
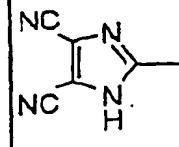
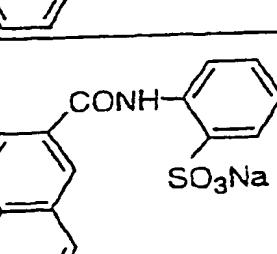
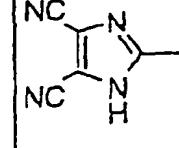
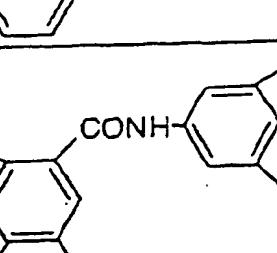
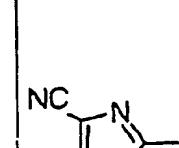
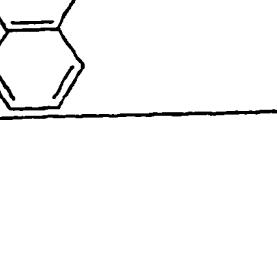
| No. | X ₁ | -Ar ₁ | Metal compound |
|------|---|---|---------------------------------------|
| 1-39 |  |  | NiCl ₂ · 6H ₂ O |
| 1-40 |  |  | NiCl ₂ · 6H ₂ O |
| 1-41 |  |  | NiCl ₂ · 6H ₂ O |
| 1-42 |  |  | NiCl ₂ · 6H ₂ O |
| 1-43 |  |  | NiCl ₂ · 6H ₂ O |

Table 1 (Cont'd)

| 5 | NO. | X1 | -Ar1 | Metal compound |
|----|------|----|------|---|
| 10 | 1-44 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 15 | 1-45 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 20 | 1-46 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 25 | 1-47 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 30 | 1-48 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 35 | | | | |
| 40 | | | | |
| 45 | | | | |
| 50 | | | | |
| 55 | | | | |

Table 1 (Cont'd)

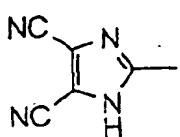
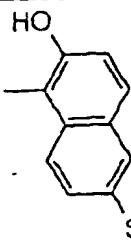
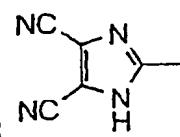
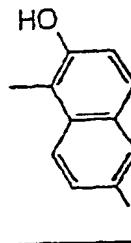
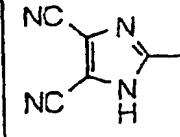
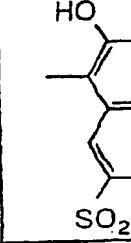
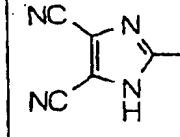
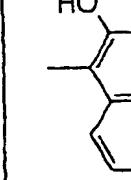
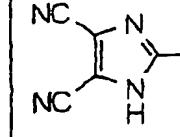
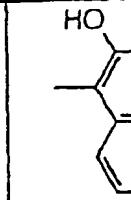
| No. |  | -Ar ₁ | Metal compound |
|------|---|--|--|
| 1-49 |  |  SO ₂ NHCH ₂ SO ₃ Na | NiCl ₂ · 6H ₂ O |
| 1-50 |  |  SO ₂ NHC ₃ H ₆ SO ₃ Na | NiCl ₂ · 6H ₂ O |
| 1-51 |  |  SO ₂ N(CH ₂ CO ₂ Na) ₂ | NiCl ₂ · 6H ₂ O |
| 1-52 |  |  CO ₂ Na | NiCl ₂ · 6H ₂ O |
| 1-53 |  |  CO ₂ Na | Ni(CH ₃ COO) ₂ · 4H ₂ O |

Table 2

| No. | | -Ar ₁ | Metal compound |
|-----|--|------------------|---|
| 2-1 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 2-2 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 2-3 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 2-4 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |

Table 2 (Cont'd)

| No. | | -Ar ₁ | Metal compound |
|-----|--|------------------|---------------------------------------|
| 2-5 | | | NiCl ₂ · 6H ₂ O |
| 2-6 | | | NiCl ₂ · 6H ₂ O |
| 2-7 | | | NiCl ₂ · 6H ₂ O |
| 2-8 | | | NiCl ₂ · 6H ₂ O |

5

10

15

20

25

30

35

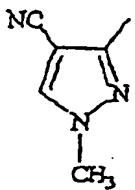
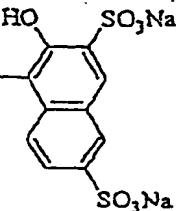
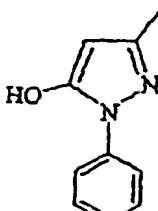
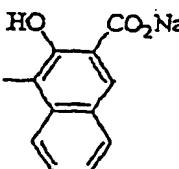
40

45

50

55

Table 2 (Cont'd)

| No. |  | -Ar ₁ | Metal compound |
|------|---|--|---------------------------------------|
| 2-9 |  |  | NiCl ₂ · 6H ₂ O |
| 2-10 |  |  | NiCl ₂ · 6H ₂ O |

30

35

40

45

50

55

Table 3

5

10

15

20

25

30

35

40

45

50

55

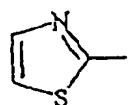
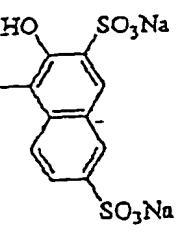
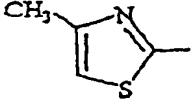
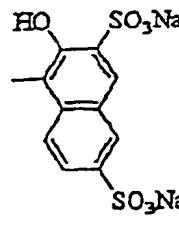
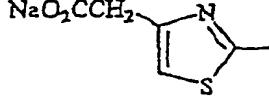
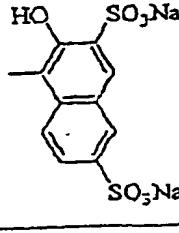
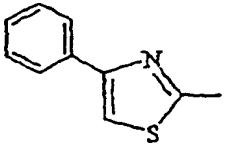
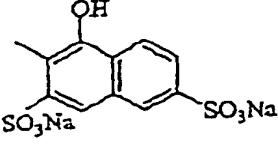
| Na |  | $-Ar_1$ | Metal compound |
|-----|---|--|-----------------------|
| 3-1 |  |  | $NiCl_2 \cdot 6 H_2O$ |
| 3-2 |  |  | $NiCl_2 \cdot 6 H_2O$ |
| 3-3 |  |  | $NiCl_2 \cdot 6 H_2O$ |
| 3-4 |  |  | $NiCl_2 \cdot 6 H_2O$ |

Table 3 (Cont'd)

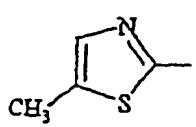
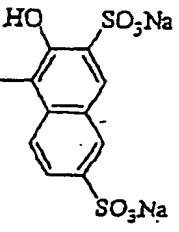
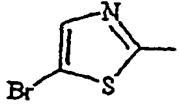
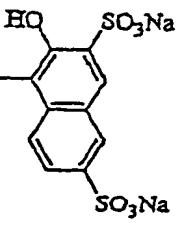
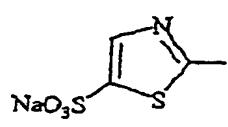
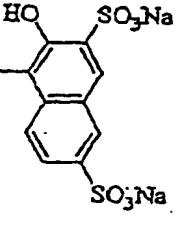
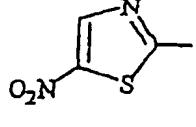
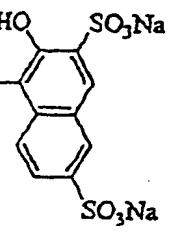
| No. |  | -Ar ₁ | Metal compound |
|-----|---|--|--|
| 3-5 |  |  | NiCl ₂ · 6 H ₂ O |
| 3-6 |  |  | NiCl ₂ · 6 H ₂ O |
| 3-7 |  |  | NiCl ₂ · 6 H ₂ O |
| 3-8 |  |  | NiCl ₂ · 6 H ₂ O |

Table 3 (Cont'd)

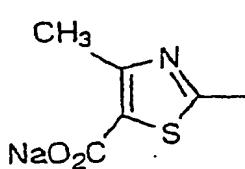
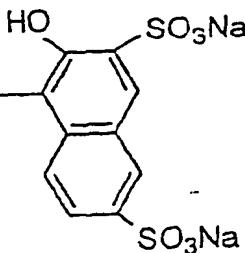
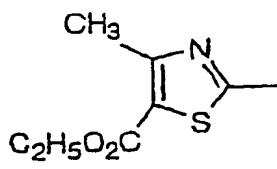
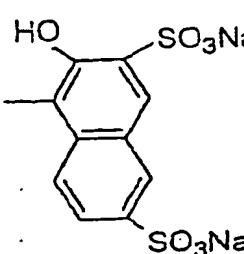
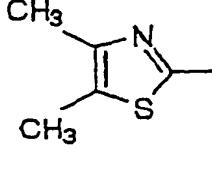
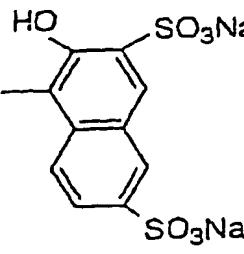
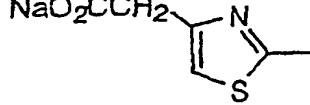
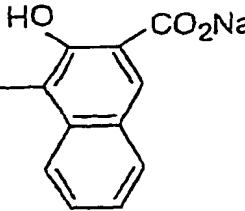
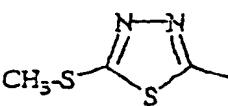
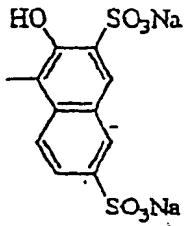
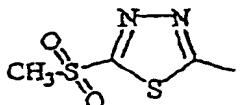
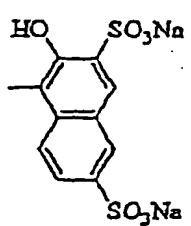
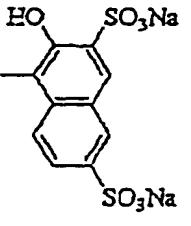
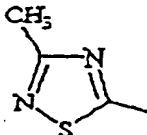
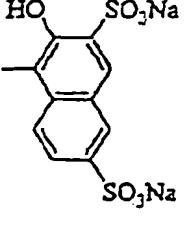
| 5 | NO. |  | -Ar ₁ | Metal compound |
|----|------|---|--|---------------------------------------|
| 10 | 3-9 |  |  | NiCl ₂ · 6H ₂ O |
| 15 | 3-10 |  |  | NiCl ₂ · 6H ₂ O |
| 20 | 3-11 |  |  | NiCl ₂ · 6H ₂ O |
| 25 | 3-12 |  |  | NiCl ₂ · 6H ₂ O |
| 30 | | | | |
| 35 | | | | |
| 40 | | | | |
| 45 | | | | |

Table 4

| No. | X_1 | $-\text{Ar}_1$ | Metal compound |
|-----|--------------|----------------|---|
| 4-1 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 4-2 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 4-3 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 4-4 | | | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |

Table 4 (Cont'd)

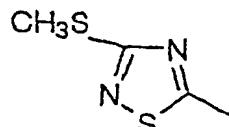
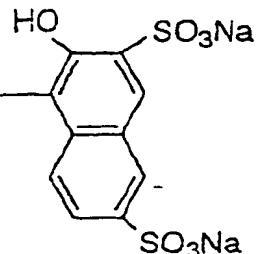
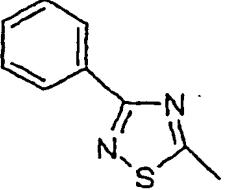
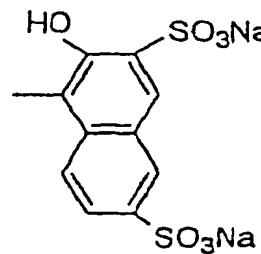
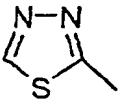
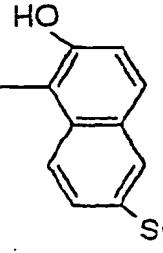
Table 4 (Cont'd)

| Na |  | -Ar ₁ | Metal compound |
|------|---|--|--|
| 4-9 |  |  | NiCl ₂ · 6 H ₂ O |
| 4-10 |  |  | NiCl ₂ · 6 H ₂ O |
| 4-11 |  |  | NiCl ₂ · 6 H ₂ O |
| 4-12 |  |  | NiCl ₂ · 6 H ₂ O |

50

55

Table 4 (Cont'd)

| NO. |  | -Ar1 | Metal compound |
|------|---|---|---|
| 4-13 |  |  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 4-14 |  |  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 4-15 |  |  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |

40

45

50

55

Table 5

Table 5 (Cont'd)

| NO. | | -Ar ₁ | Metal compound |
|-----|--|------------------|---------------------------------------|
| 5-5 | | | NiCl ₂ · 6H ₂ O |
| 5-6 | | | NiCl ₂ · 6H ₂ O |
| 5-7 | | | NiCl ₂ · 6H ₂ O |
| 5-8 | | | NiCl ₂ · 6H ₂ O |

Table 6

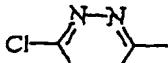
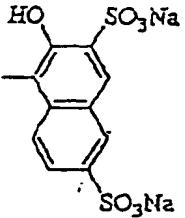
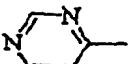
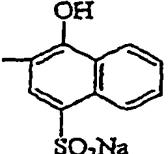
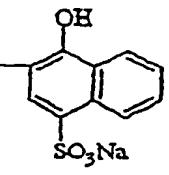
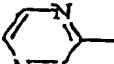
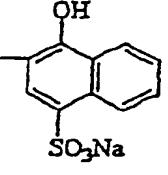
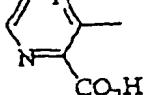
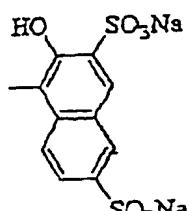
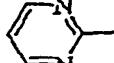
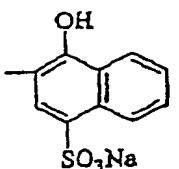
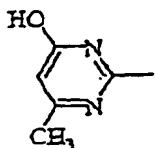
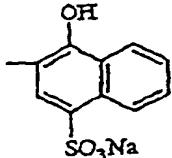
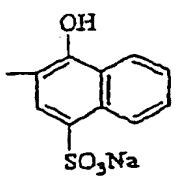
| No. |  | -Ar ₁ | Metal compound |
|-----|---|--|---|
| 6-1 |  |  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 6-2 |  |  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 6-3 |  |  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 6-4 |  |  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ |

Table 6 (Cont'd)

| No. |  | -Ar ₁ | Metal compound |
|-----|---|--|--|
| 6-5 |  |  | NiCl ₂ · 6 H ₂ O |
| 6-6 |  |  | NiCl ₂ · 6 H ₂ O |
| 6-7 |  |  | NiCl ₂ · 6 H ₂ O |
| 6-8 |  |  | NiCl ₂ · 6 H ₂ O |

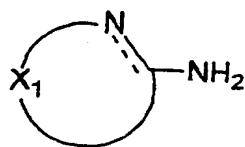
[0037] The azo metal chelated compound which is a water soluble dyestuff of the invention can be produced from an azo compound represented by the general formula (1) and a metal compound.

[0038] The azo compound represented by the general formula (1) is obtained according to a known method.

(Method A) Diazo coupling method

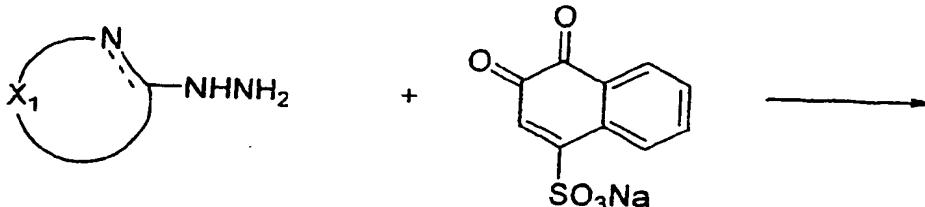
[0039] A method which comprises the diazotization of the following compound:

5



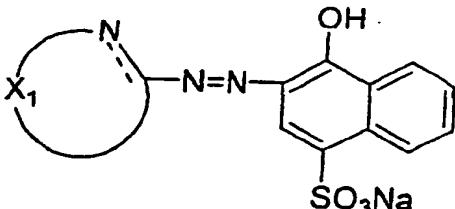
10 and coupling with H-Ar₁. Alternatively (Method B), the compound is obtained according to the method condensing a hydrazino compound with a 1,2-naphthoquinone derivative.

15



20

25



30

[0040] The water soluble azo metal chelated compound which is a compound of the invention can be produced by reacting the resulting azo dyestuff of the general formula (1) with a metal compound (e.g., NiCl₂·6H₂O, CuCl₂·2H₂O, or the like).

35 [0041] As the content of the water soluble dyestuff which is an azo chelated compound of the azo compound of the above general formula (1) with a metal in the recording liquid, the content of a deep color ink is preferably from 0.5 to 5% by weight, particularly from 2 to 4.5% by weight in total, relative to the total amount of the recording liquid. In the case that a pale color ink is used, the content of the dyestuff is preferably from 0.1 to 2% by weight, more preferably 0.1 to 1.5% by weight.

40 [0042] Moreover, the aqueous medium for use in the invention preferably contains water and, as a water soluble organic solvent, ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol (weight average molecular weight: about 190 to 400), glycerol, N-methylpyrrolidone, N-ethylpyrrolidone, 1,3-dimethylimidazolidinone, thiodiethanol, dimethyl sulfoxide, ethylene glycol monoallyl ether, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, 2-pyrrolidone, sulfolane, ethyl alcohol, isopropanol, or the like, for example. These water soluble organic solvents are used usually in the range of 1 to 45% by weight relative to the total amount of the recording liquid. On the other hand, water is used in an amount of 50 to 95% by weight relative to the total amount of the recording liquid.

45 [0043] The quick-drying property and print quality after printing can be further improved by adding, to the recording liquid of the invention, 0.1 to 10% by weight, preferably 0.5 to 5% by weight of a compound selected from urea, thiourea, biuret, and semicarbazide relative to the total amount of the recording liquid or by adding 0.001 to 5% by weight of a surfactant relative to the total amount of the recording liquid.

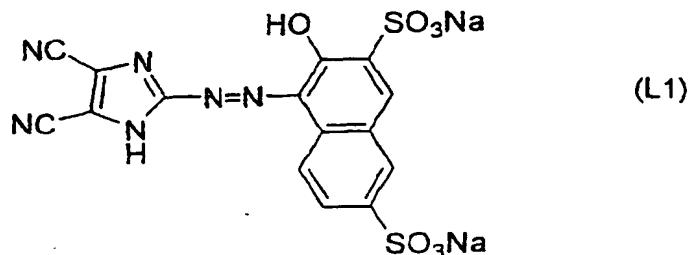
Examples

55 [0044] The following will explain the invention further in detail with reference to Examples, but the invention is not limited to these Examples unless the gist of the invention is exceeded.

<<Diazo Coupling Example 1>>

5 [0045] A solution of water (206 ml), 35% hydrochloric acid (20 ml), and 2-amino-4,5-dicyanoimidazole (10.0 g) was cooled and an aqueous solution of sodium nitrite (5.5 g) dissolved in water (12 ml) was added thereto at 5 to 10°C to effect diazotization.

10 [0046] An excess sodium nitrite was decomposed by sulfamic acid to obtain a diazo solution. Disodium 2-naphthol-3,6-disulfonate (27.5 g) was dissolved in water (284 ml), and the above diazo solution was added dropwise thereto at 0 to 5°C with adjusting the pH to 8.0 to 9.0 with an aqueous NaOH solution. The solid mass formed was collected by filtration, washed with water, and dried to obtain the dyestuff represented by the following structural formula (L1) (34.1 g).



(Example 1)

25 Preparation of a nickel chelated dyestuff

30 [0047] Water (45 ml) was added to the azo dyestuff (3.0 g) of the structural formula (L1) and the dyestuff was dissolved by adjusting the pH to 10.0 with an aqueous NaOH solution. A solution of nickel(II) chloride-hexahydrate (0.72 g)/water (7 ml) was added dropwise thereto at 15 to 25°C. During the reaction, the pH was adjusted to 9.0 to 10.0 with an aqueous NaOH solution. Sodium chloride (1.0 g) was added and solid mass was collected by filtration. The resulting wet cake was dissolved by adding water (45 ml) and heating the whole to 50 to 55°C, followed by filtration.

35 [0048] To the resulting filtrate was added isopropyl alcohol (130 ml), and precipitate was collected by filtration and dried to obtain the nickel chelated compound of No. 1-5 in Table 1 (1.1 g).

[0049] The maximum absorption wavelength (in water) of the resulting nickel chelated dyestuff was found to be 529.0 nm.

(Example 2)

40 Preparation of a copper chelated dyestuff

45 [0050] Water (300 ml) was added to the azo dyestuff (10.0 g) of the structural formula (L1) and the dyestuff was dissolved by adjusting the pH to 10.0 with an aqueous NaOH solution. Then, a solution of copper(II) chloride-dihydrate (1.73 g)/water (33 ml) was added dropwise thereto. During the reaction, the pH was adjusted to 9.0 to 10.0 with an aqueous NaOH solution. Sodium chloride (20 g) was added and solid mass was collected by filtration. The resulting wet cake was dissolved in water and isopropyl alcohol was added. Precipitate was collected by filtration and dried to obtain the copper chelated compound of No. 1-6 in Table 1 (5.0 g).

[0051] The maximum absorption wave-length (in water) of the resulting copper chelated dyestuff was found to be 544.0 nm.

50 (Examples 3 to 19)

Preparation of nickel chelated dyestuffs

55 [0052] According to methods similar to Example 1, the following nickel chelated dyestuffs were produced: No. 1-9, No. 1-10, No. 1-14, No. 1-15, No. 1-34, No. 1-36, No. 1-38, No. 1-44, No. 1-45, No. 1-46, No. 1-48, No. 1-51, No. 1-52, No. 1-53 in Table 1; No. 5-5, No. 5-8 in Table 5; No. 6-8 in Table 6.

[0053] The maximum absorption wavelengths in water of these chelated dyestuffs were measured. The chelated dyestuff used in each Example and the maximum absorption wavelength in water were shown in following Table 7.

Table 7

| Example No. | Dyestuff No. | Maximum absorption wavelength (in water) (nm) |
|-------------|--------------|---|
| Example 1 | No. 1-5 | 529.0 |
| Example 2 | No. 1-6 | 544.0 |
| Example 3 | No. 1-9 | 521.0 |
| Example 4 | No. 1-10 | 525.5 |
| Example 5 | No. 1-14 | 531.0 |
| Example 6 | No. 1-15 | 528.5 |
| Example 7 | No. 1-34 | 514.0 |
| Example 8 | No. 1-36 | 518.0 |
| Example 9 | No. 1-38 | 528.0 |
| Example 10 | No. 1-44 | 517.5 |
| Example 11 | No. 1-45 | 528.0 |
| Example 12 | No. 1-46 | 512.0 |
| Example 13 | No. 1-48 | 513.0 |
| Example 14 | No. 1-51 | 521.0 |
| Example 15 | No. 1-52 | 519.0 |
| Example 16 | No. 1-53 | 517.0 |
| Example 17 | No. 5-5 | 577.0 |
| Example 18 | No. 5-8 | 562.5 |
| Example 19 | No. 6-8 | 561.5 |

[0054] Moreover, mass spectrum of No. 1-34 was measured on a magnetic field-type mass spectrometer (JMS-700 manufactured by JEOL) according to an electrospray-ion method. Main peak, m/e = 791 was observed and this was coincident with the metal:azo compound = 1:2 complex of No. 1-34 (molecular weight: 792 ^{58}Ni).

(Example 20)

Preparation of a copper chelated dyestuff

[0055] According to a method similar to Example 2, a copper chelated dyestuff of No. 1-35 in Table 1 was produced.
 [0056] The maximum absorption wavelength (in water) of the resulting copper chelated dyestuff was found to be 549.5 nm.

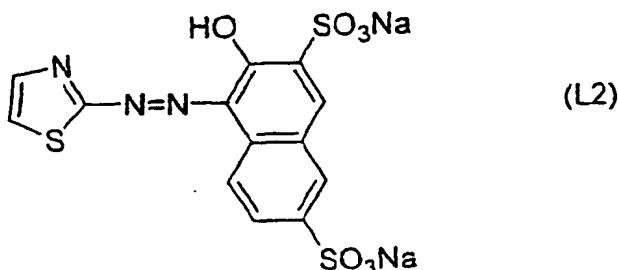
<<Diazo Coupling Example 2>>

[0057] Acetic acid (40 ml) and n-propionic acid (15 ml) were added to 2-aminothiazole sulfate (2.96 g) and the whole was cooled to -5°C. Under stirring at 0 to -5°C, nitrosyl sulfate (43.8%, 6.4 g) was added thereto and the whole was stirred to obtain a diazo solution. The diazo solution thus obtained was added to disodium 2-naphthol-3,6-disulfonate (7.0 g) dissolved in ice-water (300 ml). Coupling was effected by adding a 20% aqueous NaOH solution at 5°C or lower and neutralizing to pH 3. Sodium chloride (40 g) was added thereto and solid mass was collected by filtration.

[0058] The resulting wet cake was re-dispersed into water (volume: 200 ml), the pH was adjusted to 9.0 with an aqueous NaOH solution, and isopropyl alcohol (300 ml) was added. Precipitated dyestuff was collected by filtration, washed with a mixture of water/isopropyl alcohol = 1/1, and dried to obtain the azo dyestuff of the following structural formula (L2) (7.48 g).

5

10



(Example 21)

15 Preparation of a nickel chelated dyestuff

[0059] Water (40 ml) was added to the dyestuff (1.53 g) of the structural formula (L2) and the dyestuff was dissolved by adjusting the pH to 10.0 with an aqueous NaOH solution. Then, an aqueous solution of nickel(II) chloride-hexahydrate (0.792 g) was added dropwise thereto. During the reaction, the pH was adjusted to 5.0 to 6.0 with acetic acid and the whole was stirred. After the disappearance of the raw material, the reaction mixture was added to isopropyl alcohol (80 ml) and precipitated dyestuff was collected by filtration, washed with a mixture of water/isopropyl alcohol = 1/2, and dried to obtain the nickel chelated dyestuff of No. 3-1 in Table 3 (1.63 g).

[0060] The maximum absorption wavelength (in water) of the resulting nickel chelated dyestuff was found to be 545.5 nm.

25

(Examples 22 to 29)

Preparation of nickel chelated dyestuffs

30 [0061] According to methods similar to Example 16, the following nickel chelated dyestuffs were produced: No. 2-6 in Table 2; No. 3-12 in Table 3; No. 4-1, No. 4-2, No. 4-15 in Table 4; No. 5-1, No. 5-2, No. 5-3 in Table 5.

[0062] The maximum absorption wavelengths in water of these nickel chelated dyestuffs were measured. The chelated dyestuff used in each Example and the maximum absorption wavelength in water were shown in following Table 8.

Table 8

35

40

45

50

| Example No. | Dyestuff No. | Maximum absorption wavelength (in water) (nm) |
|-------------|--------------|---|
| Example 20 | No. 1-35 | 549.5 |
| Example 21 | No. 3-1 | 545.5 |
| Example 22 | No. 2-6 | 521.5 |
| Example 23 | No. 3-12 | 554.5 |
| Example 24 | No. 4-1 | 531.0 |
| Example 25 | No. 4-2 | 527.5 |
| Example 26 | No. 4-15 | 527.5 |
| Example 27 | No. 5-1 | 504.5 |
| Example 28 | No. 5-2 | 507.0 |
| Example 29 | No. 5-3 | 561.0 |

(Example 30)

55 Preparation of a recording liquid

[0063] Water was added to 10 parts by weight of diethylene glycol, 3 parts by weight of diethylene glycol monobutyl ether, and 3.0 parts by weight of the above nickel chelated dyestuff of No. 1-5 obtained in Example 1, and the pH was

adjusted to 9 with an aqueous sodium hydroxide solution to make the total amount 100 parts by weight. The composition was thoroughly mixed to dissolve the components. After filtration under pressure through a Teflon (a registered trademark) filter having a pore size of 1 μm , the filtrate was subjected to a degassing treatment by means of a vacuum pump and an ultrasonic cleaner to prepare a recording liquid.

[0064] Using the resulting recording liquid, inkjet recording was conducted on each of an electrophotographic paper (Brand name: 4024 paper, a product of Xerox Corporation), a super fine specialized paper (Brand name: MJA4SP1, manufactured by Seiko Epson Corporation), a super fine specialized glossy paper (Brand name: MJA4SP3, manufactured by Seiko Epson Corporation), and a specialized photoprint paper (Brand name: PMA4SP1, manufactured by Seiko Epson Corporation) with an inkjet printer (Brand name: PM-750C, a product of Seiko Epson Corporation). The saturation of the resulting printed matter was measured by Macbeth densitometer (Gretag Macbeth SPM50, manufactured by Macbeth), and quantified as the form of a C^* value. Incidentally, the C^* value is a numerical value expressing the height or lowness of the saturation of an image. That is, the larger the value is, the higher the saturation is. In the case of the specialized photoprint paper, a good result was obtained at the above measurement wherein the C^* value was 77.8. Also, several evaluations were conducted according to the following methods of (a) to (c).

(a) Light resistance of a recorded image:

[0065] Using a xenon fade-meter (manufactured by Atlas), a recording paper was irradiated at an irradiation energy of 150 to 160 kJ/m^2 for 80 hours, and the degree of discoloring and fading before and after the irradiation was measured by Macbeth densitometer (Gretag Macbeth SPM50, manufactured by Macbeth), and quantified as the form of a ΔE value. Incidentally, the ΔE value is a numerical value expressing the degree of discoloring and fading. That is, the larger the value is, the larger the degree of discoloring and fading is and the lower the light fastness of the image is. In the case of the specialized photoprint paper, a good result was obtained at the above measurement wherein the ΔE value was 2.1.

(b) Indoor discoloring and fading property of a printed image (ozone resistance):

[0066] In a light-shielded tank having an ozone concentration of 3 ppm, a printed matter was left on standing under a humidity of 50 to 60 % for 2 hours, and the degree of discoloring and fading before and after the standing was measured by Macbeth -densitometer (Gretag Macbeth SPM50, manufactured by Macbeth), and quantified as the form of a ΔE value. In the case of the specialized photoprint paper, a good result was obtained at the above measurement wherein the ΔE value was 11.2.

(c) Storage stability of a recording liquid:

[0067] A recording liquid was placed in a container made of Teflon (a registered trademark) and it was tightly closed. Upon the examination after one month storage at 5°C and 60°C, no precipitation of insoluble matter was observed.

(Examples 31 to 39)

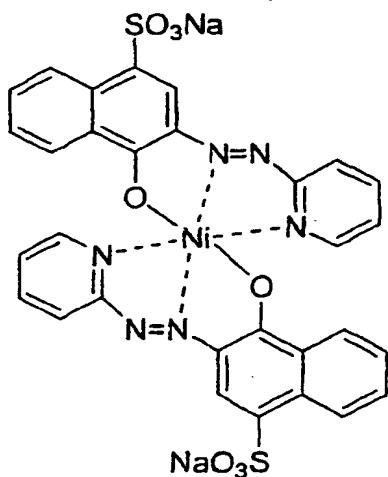
Preparation of recording liquids

[0068] Recording liquids were prepared in a similar manner to Example 30 with the exception that azo metal chelated compounds produced in Examples 2, 3, 5, 7, 8, 12, 13, 14, and 15 were used instead of the dyestuff used in Example 30, and printing was conducted in a similar manner to Example 30.

[0069] Also, the evaluations according to the methods of (a) to (c) were conducted in a similar manner to Example 30 to obtain good results in all evaluations as shown in Table 9 in the case of the specialized photoprint paper.

(Comparative Example 1)

[0070] A recording liquid was prepared in a similar manner to Example 30 with the exception that the dyestuff represented by the following formula (Comparative dyestuff a):



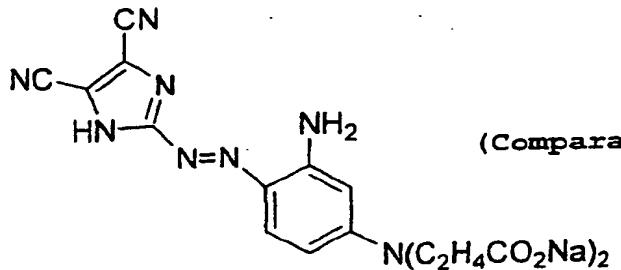
(Comparative dyestuff a)

20 described in Example 1 of Japanese Patent Laid-Open No. 140367/1999 was used instead of the dyestuff used in Example 30. In a similar manner to Example 30, printing was conducted and the saturation of the resulting printed matter was measured. The evaluations according to the methods of (a) to (c) were conducted in a similar manner to Example 30 to obtain results as shown in Table 9 in the case of the specialized photoprint paper.

25 [0071] The dyestuff in Example 1 of Japanese Patent Laid-Open No. 140367/1999 is an azo metal chelated compound having a pyridine ring and it is understood that the compound is extremely inferior to the compounds of the invention in indoor discoloring and fading property.

(Comparative Example 2)

30 [0072] A recording liquid was prepared in a similar manner to Example 30 with the exception that Ni (II) complex of the dyestuff represented by the following formula (Comparative dyestuff b):



(Comparative dyestuff b)

falling within the range of Japanese Patent Laid-Open No. 259331/1998 was used instead of the dyestuff used in Example 30. In a similar manner to Example 30, printing was conducted and the saturation of the resulting printed matter was measured. The evaluations according to the methods of (a) to (c) were conducted in a similar manner to Example 30 to obtain the results as shown in Table 9 in the case of the specialized photoprint paper.

50 [0073] The azo metal chelated compound used in Comparative Example 2 is one having a benzene ring and it is understood that the compound is extremely inferior in the saturation to the compounds of the invention having a naphthalene ring.

Table 9

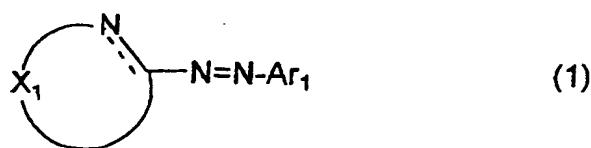
| Example No. | Dyestuff No. | Saturation (C*) | Light resistance (ΔE) | Indoor discoloring & fading property (ΔE) |
|-----------------------|------------------------|-----------------|---------------------------------|---|
| Example 30 | No. 1-5 | 77.8 | 2.1 | 11.2 |
| Example 31 | No. 1-6 | 76.3 | 2.4 | 13.6 |
| Example 32 | No. 1-9 | 67.7 | 1.3 | 3.9 |
| Example 33 | No. 1-14 | 75.7 | 2.6 | - |
| Example 34 | No. 1-34 | 72.3 | 1.3 | 4.9 |
| Example 35 | No. 1-36 | 71.5 | 1.8 | 6.8 |
| Example 36 | No. 1-46 | 72.8 | 11.0 | 11.2 |
| Example 37 | No. 1-48 | 73.7 | 3.0 | 2.5 |
| Example 38 | No. 1-51 | 74.7 | 3.7 | 2.2 |
| Example 39 | No. 1-52 | 71.7 | 1.2 | 11.3 |
| Comparative Example 1 | Comparative dyestuff a | 69.4 | 4.4 | 17.8 |
| Comparative Example 2 | Comparative dyestuff b | 42.8 | 7.0 | 4.3 |

25 Industrial Applicability

[0074] The dyestuff of the invention is excellent in the solubility in water. When the recording liquid using the dyestuff is employed, as an aqueous inkjet recording liquid, for printing on a plain or specialized paper, a clear recorded matter can be obtained and the dyestuff exhibits an excellent print density, light resistance, and indoor discoloring and fading property, and also a good storage stability as a recording liquid.

Claims

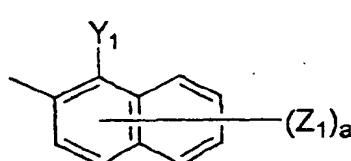
35 1. A metal chelated dyestuff for inkjet recording which is a water soluble azo metal chelated compound formed from an azo compound represented by the following general formula (1) and a metal element:



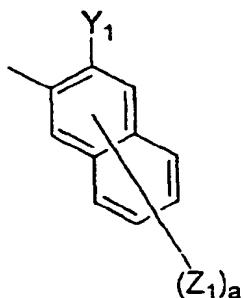
45

(where general formula (1) represents an azo dyestuff compound having at least one or more hydrophilic groups in a molecule, X_1 represents plural atoms required for forming at least one 5- to 7-membered heterocyclic ring, the heterocyclic ring containing X_1 being a heterocyclic ring other than pyridine ring, The heterocyclic ring containing X_1 may have substituent(s) on the heterocyclic ring, the substituent(s) on the heterocyclic ring may form a condensed ring through further condensation, The condensed heterocyclic ring containing X_1 may be substituted, Ar_1 represents naphthyl group represented by the following general formulae (2) - (4), Y_1 represents a chelating group, Z_1 represents any substituent which may be different from each other, and a represents an integer of 0 to 6)

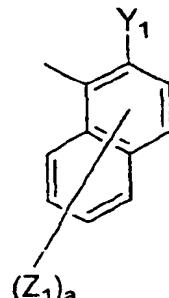
55



(2)



(3)



(4)

2. A metal chelated dyestuff for inkjet recording as defined in claim 1, wherein the heterocyclic ring containing X_1 in the general formula (1) is imidazole ring, pyrazole ring, isoxazole ring, thiazole ring, thiadiazole ring, pyridazine ring, pyrimidine ring, pyrazine ring, benzothiazole ring, benzoxazole ring, or benzimidazole ring.

3. A metal chelated dyestuff for inkjet recording as defined in claim 1 or 2, wherein in the general formula (1) the heterocyclic ring containing X_1 may have one or more substituents, each substituent on the heterocyclic ring being a group which is independent of each other selected from the group consisting of alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, allyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxycarbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carbamoyl group which may be substituted, acyl group which may be substituted, carboxyl group, hydroxyl group, cyano group, acylamino group which may be substituted, nitro group, halogen atom, phosphono group, sulfo group, mercapto group, alkylthio group which may be substituted, alkylsulfonyl group which may be substituted, alkylsulfonyl group which may be substituted, and thiocyanato group.

4. A metal chelated dyestuff for inkjet recording as defined in any one of claims 1 to 3, wherein in the general formulae (2) to (4), Y_1 represents hydroxyl group, carboxyl group, amino group which may be substituted, sulfo group, carbamoyl group, alkoxy group which may be substituted, alkylthio group which may be substituted, alkylsulfonylamino group which may be substituted, or arylsulfonylamino group which may be substituted.

5. A metal chelated dyestuff for inkjet recording as defined in any one of claims 1 to 4, wherein in the general formulae (2) to (4), each Z_1 represents independently alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxycarbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carbamoyl group which may be substituted, hydroxyl group, amino group which may be substituted, ureido group, acylamino group which may be substituted, alkylsulfonylamino group which may be substituted, arylsulfonylamino group which may be substituted, phosphono group, sulfo group or sulfamoyl group which may be substituted.

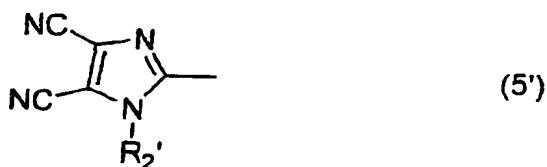
6. A metal chelated dyestuff for inkjet recording as defined in any one of claims 1 to 5, wherein in the general formula (1), the heterocyclic ring containing X_1 is represented by the following general formula (5):



55 (where R_1 may be different from each other and is a group selected from alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted,

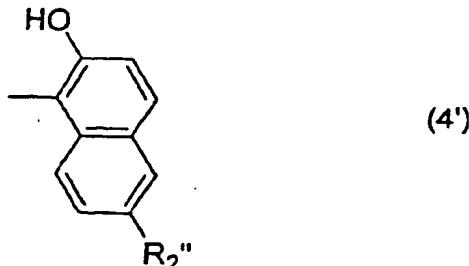
tuted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxycarbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carboxyl group, carbamoyl group which may be substituted, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, mercapto group, alkylthio group which may be substituted and thiocyanato group. R₁ may further form a condensed ring together with an imidazole ring, c represents an integer of 0 to 2; R² represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted and allyl group which may be substituted.)

10 7. A metal chelated dyestuff for inkjet recording as defined in claim 6, wherein the general formula (5) is the following general formula (5'):



20 (where R_2' represents hydrogen atom or alkyl group which may be substituted.)

8. A metal chelated dyestuff for inkjet recording as defined in claim 7, wherein Ar_1 is represented by the following general formula (4'):



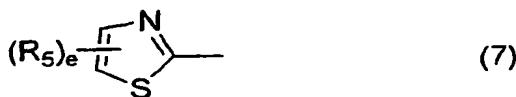
(where R_2'' represents sulfo group or sulfamoyl group which may be substituted.)

9. A metal chelated dyestuff for inkjet recording as defined in any one of claims 1 to 5, wherein in the general formula (1), the heterocyclic ring containing X_1 is represented by the following general formula (6):



50 (where R_3 may be different from each other and represents alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxycarbonyl group which may be substituted, carboxyl group, carbamoyl group which may be substituted, hydroxyl group, cyano group or sulfo group, d represents an integer of 0 to 2; R_4 represents hydrogen atom, alkyl group which may be substituted or aryl group which may be substituted.)

55 10. A metal chelated dyestuff for inkjet recording as defined in any one of claims 1 to 5, wherein in the general formula (1), the heterocyclic ring containing X_1 is represented by the following general formula (7):



10 (where R_5 may be different from each other and represents alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, alkoxy group which may be substituted, aryloxy group which may be substituted, acyloxy group which may be substituted, alkoxy carbonyl group which may be substituted, aryloxy carbonyl group which may be substituted, carboxyl group, hydroxyl group, acyl group which may be substituted, cyano group, acylamino group which may be substituted, nitro group, halogen atom, sulfo group, alkylthio group which may be substituted or arylthio group. R_5 may further form a condensed ring together with thiazole ring, e represents an integer of 0 to 2.)

15 11. A metal chelated dyestuff for inkjet recording as defined in any one of claims 1 to 5, wherein in the general formula (1), the heterocyclic ring containing X_1 is represented by the following general formula (8):



25 (where R_6 represents hydrogen atom, alkyl group which may be substituted, aryl group which may be substituted, aralkyl group which may be substituted, mercapto group, alkylthio group which may be substituted, alkylsulfoxy group which may be substituted or alkylsulfonyl group which may be substituted.)

30 12. A metal chelated dyestuff for inkjet recording as defined in any one of claims 1 to 10, wherein the water soluble azo metal chelated compound is a water soluble azo metal chelated compound formed from a metal element selected from nickel, copper and cobalt.

13. An aqueous inkjet recording liquid containing an aqueous medium and at least one or more metal chelated dyestuffs as defined in any one of claims 1 to 10.

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/09041

A. CLASSIFICATION OF SUBJECT MATTER
Int.C1' C09B45/14, C09D11/00, B41MS/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.C1' C09B45/14, 45/18, 45/20, 45/22, C09D11/00,
B41MS/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
REGISTRY (STN) CASPLUS (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|--------------------------|
| Y A | JP, 11-5931, A (HODOGAYA CHEMICAL CO., LTD.), 12 January, 1999 (12.01.99) (Family: none) | 1-5,9,12,13 6-8,10,11 |
| Y A | US, 4962191, A (CIBA GEIGY AG), 09 October, 1990 (09.10.90) & EP, 357554, A1 & JP, 2-117962, A | 1,5,12,13 2-4,6-11 |
| Y A | EP, 481449, A2 (SUMITOMO CHEM CO LTD), 22 April, 1992 (22.04.92), page 8, lines 7, 22 & JP, 4-153272, A & JP, 4-285677, A & US, 5183501, A & DE, 69118302, E | 1,3-5,12,13 2,6-11 |
| Y A | US, 5102459, A (HOECHST AG), 07 April, 1992 (07.04.92). Columns 7, 8(1e) & EP, 312004, A1 & DE, 3734528, A & JP, 1-123866, A | 1-5,9,12,13 6-8,10,11 |
| Y A | JP, 58-176267, A (Canon Inc.), 15 October, 1983 (15.10.83) (Family: none) | 1-5,9,12,13 6-8,10,11 |

 Further documents are listed in the continuation of Box C. See patent family annex.

| | |
|---|--|
| • Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family |
|---|--|

Date of the actual completion of the international search
09 March, 2001 (09.03.01)Date of mailing of the international search report
27 March, 2001 (27.03.01)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/09041

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|--|-------------------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y A | JP, 10-259331, A (Konica Corporation), 29 September, 1998 (29.09.98) (Family: none) | 1-5, 9, 12, 13 6-8, 10, 11 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)